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# SOLVENTLESS, CURABLE FLUID OLIGOMERIC SYSTEMS FOR HIGH PERFORMANCE MICROWAVE, ACOUSTICAL AND MECHANICAL APPLICATIONS

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## ABSTRACT

While establishing the basis for our "Technology 2000" product plan several years ago we plugged in the usual factors contributing toward product success.

- Price/performance justifiable
- Profitable, warranting high quality maintenance, enhancement and specific property improvement
- Narrow inventory requirements
- Raw material integrable backwards with easily variable properties (molecular weight, functionality, isomer control)

We resolved this by selecting radical functional, low molecular weight polybutadiene liquid polymers. Encouraged by the need for solid rocket binders several companies embarked on various perceptions of binder performance requirements over four decades ago. Initially dominated by progress of liquid polysulfides[1] soon a few settled primarily upon polybutadiene based binders.[2] Such an approach in a few instances was exploited quite viably with a series of functional group terminated liquid polybutadienes; hydroxyl, mercaptan, carboxyl, vinyl and amine. Our attention was directed to oligomers, liquid polymers and their hybrids. As you will see, the results have been spectacular. The only significant limits on compounded products has been solvent resistance and oxidative sensitivity, unless sufficient proportion of sulfide or nitrile moiety is incorporated. For convenience we have grouped them under the trademarks Nylane, Seamax, Oligomax, and Castomax all with a certain flair of acronymical significances.

## GENERAL SYSTEM TECHNIQUES

The versatility of our complex oligomers may best be seen from the diverse summary of applications performance properties in Figure 1.

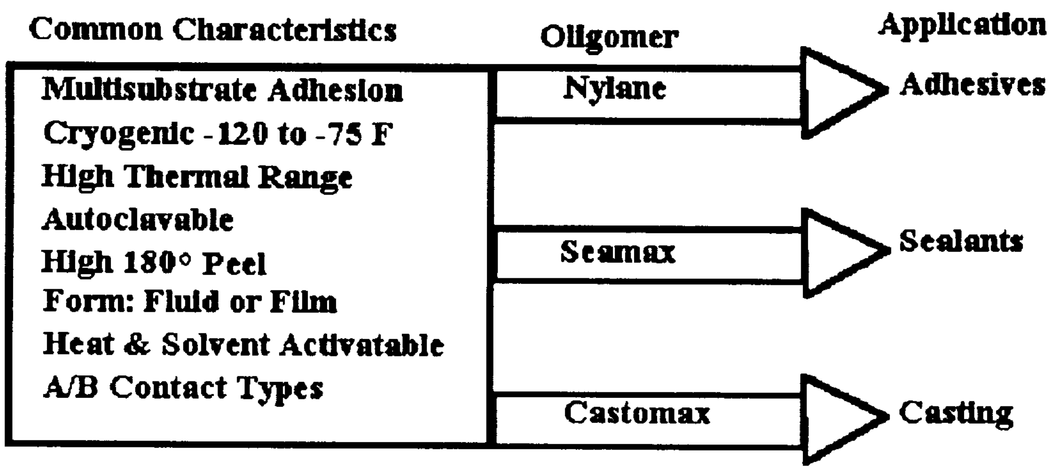



FIGURE 1

The abbreviated non-linear presentation in Figure 1 has proved quite useful in new product conception, development and improvement. Table 1 provides the functionality and process tools to arrive at targeted end product properties and performances for designed applications.

TABLE 1

| RADICAL FUNCTIONALITIES | REACTION PROCESSES |
|---|---|
| Mercaptan | Vinyl addition, oxidation |
| Amine | Addition, Ionic, condensation |
| Unsaturation | Free radical, thermal/chemical |
| Silane | Hydrolysis, Addition |
| Isocyanate | Addition, Condensation Sterically, selective Isocyanurization |
| Ester | Transamination |
| Epoxide | Addition, auto polymerization |

Exploratory work indicates a useful computer program is feasible using linear and random approaches.

## APPLICATIONS

### Foams, Sprayed-in-Place

The utilization of low density coatings is widespread in the aerospace industry. Historically, coatings of this type have been fabricated as syntactic foams in an attempt to meet the density, thermal conductivity, and/or electrical properties required. These coatings have significant deficiencies from many aspects including toughness, minimum density limits, cost and environmental problems. An alternative are blown foam coatings that match or exceed the mechanical, environmental, electrical and physical properties of the syntactic foam coatings.

Syntactic foam coatings consist of thermoset resin systems that have been loaded with fillers called microballoons to significantly lower the density of the coating. This in turn adjusts certain properties such as the dielectric constant and/or thermal conductivity of the coating to obtain a desired effect. The microballons utilized are typically either a hollow glass sphere or a hollow polymer sphere and by adding a specified quantity of these spheres to the thermoset resin a low density coating with the desired properties can be obtained.

The loading of large quantities of microballoons into thermoset resin systems severely degrades the mechanical properties and significantly increases the process problems associated with utilizing the thermoset resin system. To make low density coatings a high percentage of the system must be comprised of the microballons which tends to degrade the mechanical strength of the coating due to a resin starved scenario. Furthermore the effect of diminishing returns arises as more microballoons are added to the system which tends to bound the lower limit of the density of the coating at approximately 0.4 g/cc (25 $lbs/ft^3$) for thermoset resin systems. In addition to the problems presented previously these systems typically require the use of significant quantities of solvents to mix the microballons into the resin system and to carry the coatings during spray applications. The initiative to lower VOC emissions has seriously restricted the use of syntactic foam coatings for this reason.

Sprayable blown foam coatings are a viable alternative to the syntactic foam coatings mentioned previously. Coatings of this type have been fabricated that have composite densities of 0.1 g/cc (6 $lbs/ft^3$). All of these coatings were sprayed without the use of a carrier solvents so the VOC content of the system was limited to the VOC content of the resin system and the blowing action taking place (if any).

A polyurethane based sprayable blown foam coating series was developed based on NYLANE casting resin[5]. This resin system was selected due to the excellent mechanical properties, durability, and availability. Nylane IV is comprised of an oligomeric polyol and in this case aliphatic isocyanurate. This isocyanate was selected for the sprayable blown foam applications due to the low viscosity and low vapor pressure which is advantageous for spraying applications. It is a slow reacting isomeric isocyanate, so numerous catalysts were obtained and screened to determine which system or systems would produce the desired cure rate(s) and coating densities desired. The blowing agent mechanism for this system is the reaction of the emerging isocyanate with water to produce carbon dioxide gas. By utilizing the water/isocyanate reaction, alternative blowing agents such as FREON based systems were not needed to produce the blown foam. Uniform application over large area metallic surfaces is possible while obtaining uniform bulk and surface mechanical - electrical properties.

Numerous applications have been identified for low density sprayable blown foam coatings. Some examples include low thermal conductivity coatings, low dielectric/low loss coatings, and lightweight abrasion resistant coatings.

### Transparent Adhesives (Seamax)

By hydrogenation with Wilkinson type platinum catalysts one can obtain two component adhesives which are optically transparent and very oxidation resistant. They are used as an adhesive to bond transparent Kynar to glass. This composite is installed in glove boxes with the Kynar facing the inside. The boxes are used for cleaning stainless steel with $HF/HNO_3$. Breaks in the Kynar often occur with sharp edges of the parts or with cleaning tools. The adhesive resists acid penetration at the cut area for at least two weeks. Glass etching is thus avoided. Optical integrity is maintained over much of the life of the boxes. Visibility from 60° sight angles are virtually undistorted. Yield per square foot is high affording low material costs. However, application costs tend to be a bit high due to the skill needed to apply the film with no trapped bubbles and uniform adhesive thickness to assure clarity. There are obviously associated applications in the chemical industry.

## Antenna Cover Bonding (Seamax 9-27C-1)

Seamax 9-27C-1 liquid adhesive was chosen for an antenna cover bonding because of its low dielectric constant and loss tangent combined with its retention of mechanical characteristics at low temperature and high humidity. Seamax is a two part polyurea-urethane hybrid adhesive. The Seamax film adhesive was evaluated for mechanical properties. Three types of tests were performed:

(1) Climbing Drum Peel Test per ASTM D1781 (indicates quantitative resistance of adhesive to combined tensile and shear loads in a honeycomb sandwich with one Duroid 5880 face sheet).

(2) Flatwise Tensile Test per ASTM C297 (indicates tensile strength of the adhesive normal to the plane of a honeycomb sandwich).

(3) Lap Shear Test per ASTM D1002 (indicates shear strength) Modifications: This test was modified to find the effect of humidity on the adhesive. One side of each of the lap shear coupons was Duroid 5880, instead of aluminum, to simulate the application.

### Climbing Drum Peel Tests

**Acceptable peel strength**: 8 pounds per linear inch
**Goal peel strength**: 20 pounds per linear inch
**Results**: 21 pounds/inch width
**Note**: Honeycomb failed

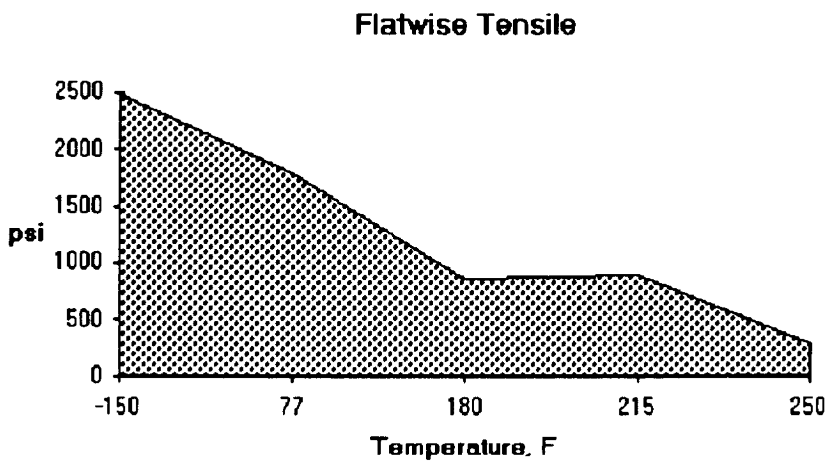
**Conclusion - Climbing Drum Peel**
The average value was higher than the goal value chosen prior to testing. This fact, coupled with the honeycomb failure, is an indication that Seamax film's resistance to peel is exceptional in the given sandwich construction. Since some of the tests resulted in honeycomb failure rather than bond failure, higher peel strength should be anticipated if denser or tougher honeycomb were to be used.

### Flatwise Tensile Test Data

**Acceptable Tensile Strength**: 200 pounds per square inch
**Goal Tensile Strength**: 1500 pounds per square inch

**Note**: Tensile strength criterion was based on flatwise tensile data from epoxy based adhesive tests performed with 3/16" cell aluminum honeycomb.

**Figure 2**




**Conclusion - Flatwise Tensile**

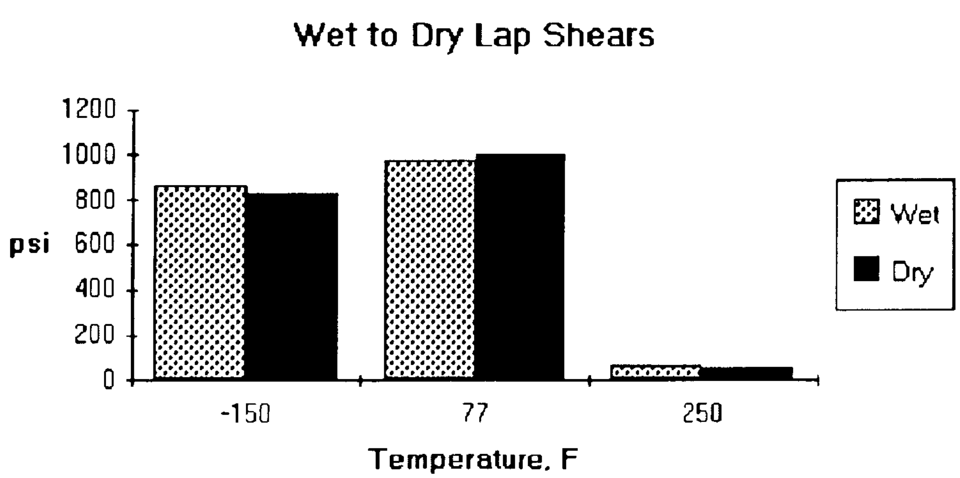
Figure 2 illustrates the excellent low temperature tensile strength of Seamax. The corrected bonding surface of the honeycomb in the 1" x 1" sandwich is 0.02925 square inches.

**Lap Shear Test Data**

**Acceptable Ratio of Strength:** Wet: Dry = 0.75:1
**Goal Ratio of Strength:** Wet: Dry = 0.95:1

Note: Samples out of humidity chamber 24 hours before testing.

**Figure 3**



## Conclusion - Lap Shear, Wet vs Dry

The wet samples at ambient temperatures for Set One and Set Two had average strengths per inch width of 234# and 239# respectfully. This means that the failure point for the adhesive, in pounds per square inch, could not be reached before the 0.060" Duroid's failure point, in pounds per inch width. With the dry samples, Duroid's failure point was only reached in Set One. The failure point for the dry Duroid is approximately 317 pounds per inch width. For Set Two the force in pounds per inch width averaged 221, so the failure point of the Duroid was never reached and data on the shear strength of the adhesive was recorded.

Because the bondline for the wet samples could not be broken, the ambient temperature tests were not conclusive. The difference in average strength at ambient temperature between the wet and the dry is only 33 psi; this number is much lower than the standard deviation for either set. The ratio of the average strength values at 77°F for the wet samples to the dry samples is 0.967:1; this ratio is higher than the goal set prior to testing. Therefore, it can be assumed that at ambient temperature, humidity does not have a large effect. At cryogenic and elevated temperatures, the average bond strength is actually greater for the wet samples.

## "7 Minute" Elastomeric Adhesive (Seamax)

A very favorable comparison may be made with mercaptan promoted "5 minute" epoxies! A Seamax type elastomer may be compounded that is very forgiving in its ability to bond to a wide variety of unprepared surfaces.

A typical application has the two component adhesive packaged in a "split" or "bi" pack for convenient containment and dispensing. The Baja 1000 served a number of years ago as an ideal field test.

One of the drivers of a dune buggy class was supplied with a few kits consisting of a hundred gram bi-pak, on application spatula, a metal brush, and a roll of polyester scrim. Fortunately (!) the driver blew a tire at forty miles out and again at 120 miles. A repair was necessary. The tear was about ten inches long and roughly followed the outside circumference of the tire. The rip was jagged. The surface was scrapped randomly for a minute, the mixed adhesive was applied to the surface and adjacent to the tear was coated generously with adhesive (slump grade). The scrim was applied over the coated area (about two inches in all direction of the tear) and pressed lightly. The remaining adhesive was then applied over the entire area. At 7 minutes the spread life was gone. At ten minutes the tire was mounted and at fifteen minutes the buggy was underway to complete the race!

## Severe Adhesive Exposure, Oligomax

Cyclic harsh laundering and autoclaving at 270°F. for 1/2 hour periods is common in health care facilities. For example, bar graphing for loss prevention of a variety of nylon, polyester, and fabric supplies such as bedding and specialized apparel as breathable surgeons gowns is laundered and often autoclaved. Also, included are many instruments autoclaved for sanitary purposes. Oligomax adhesives functioning as the adhesive in composite tapes consisting of an imprinted fabric or metal tape, adhesive, and release film in the usual roll form is easily steam or heat activated for permanent application.

Breathable composite apparel has been assembled by B-stage preforms, steam activated, fully or partially cured for additional down-stream processing. Currently, this B-staging shows exceptional promise for continuous belt fabrication because of its bonding strength (Kevlar and steel) members.

**Potting and Molding, Castomax**

Commercial acceptance of a series of oligomers for acoustical sensor device protection. A number of desirable properties virtually assures their success.

Exceptional safety in handling and use
Excellent primerless adhesion
Excellent water resistance
User friendly, favorable Reynold's Number
Density close to water and variable
Rho C = ~ $1597^{6}$ and tunable,
Variable work life from 10 to 90 minutes

## SUMMARY

A collage of liquid polymers has been developed with wide-ranging applications. The products are variations of polybutadiene oligomers involving free radical and addition cross-linking and chain extension via several different radical functionalities such as amine, silicone, isocyanate and others.

The mechanical properties of the resultant cured polymers cover a range from viscoelastic fluids through elastomers, elastoplastic fluids through elastomers, elastoplastics and plastics. They have in common unusual mechanical and electric properties with outstanding water resistance. Furthermore evidence was shown that the development of products with engineered features which were not possible to produce heretofore. For instance, microwave antennas may be assembled with efficiencies over 95% while maintaining or advancing all antenna functions. Nylane demonstrates similar broad versatility with plastic mechanical performance. They may be described as solventless, liquid curable engineering plastics. It may reasonably be anticipated that further commercial products will continue to flow from this fascinating area of materials.

## REFERENCES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(6) E.W. Thomas, USRD Tech Note 11, Rho C Value, October, 1982